

# **Sampling protocols and measurements used during the Venice cruises periode (2015 – 2017)**

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## **1. Bottom water sampling and analyses**

With the water column samples, Temperature was measured using a thermometer with a precision of 0.1 °C and salinity with a thermos-salinometer with a precision of 0.1. pH measurements were carried out in triplicate within 1 hour after sampling by spectrophotometry with unpurified m-cresol purple as indicator dye (Clayton and Byrne, 1993). They are reported on the total proton scale (pHT) with an uncertainty of  $\pm 0.01$  pH units. Dissolved oxygen concentrations were analysed by Winkler titration (Grasshoff et al., 1983) with a precision of  $\pm 0.5$   $\mu\text{M}$ .

## **2. Porosity, organic carbon content and grain size**

Sediment porosity profiles were determined by slicing one of the cores with a 2 mm resolution until 10 mm depth, a 5 mm resolution until 60 mm, and a 10 mm resolution down to the bottom of the cores. Porosity was calculated from the bottom water salinity, an average sediment density of 2.65 g cm<sup>-3</sup> and the weight difference between the wet and dried sediment after one week at 60 °C.

Organic carbon was measured after removal of inorganic carbon by hydrochloric acid until the absence of bubbling upon acid addition, followed by rinsing and centrifuging. Measurements were performed on a Fisons Instrument NA 1500 Element Analyzer at LSCE (Cathalot et al., 2013) with a precision of 0.1% dry weight.

Grain-size distribution measurements of carbonate- and organic-free terrigenous particles in the range of 1.0–2000  $\mu\text{m}$  were carried out on a Malvern Mastersizer 2000 Particle Size Analyzer at the Laboratoire Géosciences Paris-Sud (GEOPS, Université Paris-Sud/Paris-Saclay). Before analyses, bulk sediment was treated successively with 0.1 N aqueous solutions of hydrogen

peroxide ( $\text{H}_2\text{O}_2$ ) and acetic acid (25%) to remove organic materials and carbonate fractions, respectively. The mixture was then rinsed several times (about 5 rinse cycles) to remove acetic acid residues and gently shaken to achieve deflocculation of sediment. The suspension was then introduced into the fluid module of the particle size analyzer. In order to diminish errors, each sample was measured 5 times and the average of these five measurements was employed to represent the grain-size distribution of each sample.

### **3. porewater microprofiles of $\text{O}_2$ , pH and $\text{H}_2\text{S}$**

A separate core was collected for carrying oxygen, pH and  $\text{H}_2\text{S}$  microprofiles using micro-electrodes (Unisense®), (Rabouille et al., 2003, Cathalot et al., 2012; Rassmann et al., 2016). 3-4 vertical depth oxygen profiles, two pH profiles and one  $\text{H}_2\text{S}$  profile were measured on cores that were maintained at in situ Temperature using a cooling device and gently bubbled with air to ensure bottom water oxygenation and stirring. Vertical profiles were measured with a 200  $\mu\text{m}$  resolution near the sediment water interface which was increased below 2cm to 500 $\mu\text{m}$ -3000 $\mu\text{m}$  (for pH and  $\text{H}_2\text{S}$ ).  $\text{O}_2$  microelectrodes were calibrated with a two-point calibration technique using bottom water  $\text{O}_2$  concentration determined by Winkler titration and the anoxic pore waters. The pH microelectrodes were calibrated using NBS buffers (pH 4.00, 7.00 and 9.00 at 20°C) for the electrode slope at in situ T and the spectrophotometrically determined pH of the bottom waters for the absolute value (pHT scale). Signal drift of  $\text{O}_2$  and pH microelectrodes during profiling was checked to be less than 5 %. Sulfide microelectrodes are Clark-type microsensors (see precise characteristics in Cathalot et al., 2012) with a platinum guard cathode to ensure a low and stable reading without sulfide. They were calibrated using  $\text{H}_2\text{S}$  standards prepared daily from a main solution and preserved with  $\text{TiCl}_3$ . The main sulfide solution was re-titrated by the classical sulfide titration every day (Grasshoff et al. 1983). The position of the sediment-water interface (SWI) for sulfide electrode was determined visually and the measurement step (initially 200  $\mu\text{m}$ ) was adapted to adequately capture the sulfide gradient and measure deeper concentrations (with a 1-3 mm step). Total sulfide (TS) was recalculated using pH and measured  $\text{H}_2\text{S}$  (Jeroschewski et al., 1996).

### **4. porewater profiles: DIC, Alk, $\text{NH}_4$ , $\text{NO}_3$ , Fedis, $\text{CH}_4$**

The extraction of sediment pore waters was conducted immediately after returning to the air-conditioned laboratory (1-2 hours after core collection) using Rhizon filters with a mean pore size of 0.1  $\mu\text{m}$  (Seeberg-Elverfeldt et al., 2005) in a glove bag flushed with  $\text{N}_2$  to create an anoxic atmosphere. Immediately after collection, pore waters were analysed for dissolved  $\text{Fe}^{2+}$

using the ferrozine technique (Stookey, 1970) and total dissolved iron concentrations the next morning after reduction of total dissolved iron with hydroxylamine. Pore water and bottom water samples were poisoned with HgCl<sub>2</sub> for TA and DIC laboratory analysis, acidified for sulphate, and stored at 4 °C until analysis in the laboratory. Subsamples for NH<sub>4</sub> and NO<sub>3</sub> were frozen. Total alkalinity was measured by open cell titration with 0.01 M HCl (Dickson et al., 2007). DIC concentrations were analyzed with a DIC analyzer (Apollo/SciTech®) on 1 ml samples as previously described (Rassmann et al., 2016). Certified reference materials were used to calibrate the TA and DIC methods (oceanic CO<sub>2</sub> measurements, Scripps Institution of Oceanography-batch n°136). The relative uncertainty for DIC and TA was  $\pm 0.5$  % of the final value. Sulphate concentrations were quantified after dilution by ion chromatography on an ICS 1000 chromatograph (Dionex) with a relative uncertainty of this method of  $\pm 1.6$  % (Rassmann et al., 2019). To measure ammonium (NH<sub>4</sub><sup>+</sup>) concentrations, samples were diluted and analysed using the indophenol blue method (Grasshof et al., 1983). The uncertainty of the method was about 5 %. Nitrate was determined using the Vanadium chloride reductant as described in Schnetger and Lehnert (2014) followed by the NEDD/sulphanilamide addition and colorimetric measurement. Precision on total NO<sub>x</sub> was around 2%.

## **5. Time series of water column monitoring data**

Real-time measurements in the waters of the Lagoon of Venice are provided by the monitoring network SAMANet, set up and managed by the local water authority (Ferrari et al., 2004). The data are transmitted to a remote central, where they undergo a quality control procedure and analysis (Ciavatta et al., 2004). The analysis carried out in the present work explored 4 stations, taken as representatives of the different areas at which the sediments were sampled (VE 02, 04, 05, 06; see Figure 1). Oxygen concentration, water temperature and salinity data were available between March 2005 and November 2017. A subset of the complete time series covering two weeks before the expedition was subsampled for characterizing the environmental conditions in the fortnight preceding the sampling campaign for the three different years. The whole time-series of oxygen saturations at the 4 stations was used to define two indicators of low oxygen : a weekly dissolved oxygen (DO) saturation value for 4 months (from June to September) averaged over the years 2005-2017, and the number of consecutive days with minimum O<sub>2</sub> values < 25% saturation. Note that due to the high summer temperature (>20°C) and the high salinity in most of the lagoon (>25‰), saturation concentrations are below 240  $\mu\text{mol/l}$ , implying that the threshold of 25% of saturation is similar the hypoxic level (2 mg/l or 62 $\mu\text{mol/l}$ ).

## 6. References

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